NEW DATA ON THE OPTICAL PROPERTIES AND THE CHEMICAL COMPOSITION OF THE PYROXENES OF S. E. MADAGASCAR[**]

H. H. Majmundar[1]

Abstract - Twenty-nine samples of pyroxenes were separated from the pyroxenites of S. E. Madagascar and studied mineralogically and chemically. The optical and physical properties were determined by analysis of the indices of refraction, birefringence, extinction angles, optic axial angles, pleochroism and specific gravity. It was found that the indices of refraction α, vary from 1.670 to 1.724, and γ, from 1.690 to 1.743. Birefringence varies from 0.013 to 0.029. Extinction angles vary from 37.5° to 46°. Optic axial angles vary from 57° to 61° (with a positive optic sign). Specific gravity varies from 3.285 to 3.682, the samples having the darker color and higher Fe content being the more dense. The most remarkable characteristic of these pyroxenes is their notable high content of Al_2O_3, varying from 7.00-10.00%. The number of Ca atoms is equal to the sum of Fe and Mg atoms. Also, the weight percentages of CaO, 24-26%, correspond to those which exist in true diopside having the formula $Ca(Mg,Fe)Si_2O_6$. On the contrary, however, the SiO_2 content in these pyroxenes is low, between 40 and 47% by weight, when it normally would be expected to fall between 49 and 55% according to the formula. In other words, compared

---

to true diopside-hedenbergite, these pyroxenes seem to have aluminum substituted for silicon.

INTRODUCTION

The pyroxenes used in this study were separated from the pyroxenites of S. E. Madagascar, which are very rich in diopside, many being mono-mineralic. They are famous for the occurrence of phlogopite and uranothorianite deposits. LACROIX (1922) was the first to describe these rocks systematically. BESAIRIE (1930) later studied the phlogopite occurrences. In 1941, LACROIX made a detailed survey of these phlogopitic pyroxenites and published first chemical analysis of these rocks. DE LA ROCHE (1956 and 1958) was the first worker to give a detailed description and interpretation of these pyroxenites. He discussed the essential regional characteristics and the principal aspects of metamorphism, granitization and the possible mode of origin.

LACROIX (1941) divided pyroxenites chemically into two groups, in general. One consists essentially only of calco-magnesian pyroxenes and phlogipite. Silico-aluminous minerals (feldspars or wernerites) are present in a far smaller amount, or are completely absent. Pyroxenites of the second group contain light colored minerals, i.e. silico-aluminous feldspar and wernerite, which are present in quite a considerable proportion and play an important role.

For convenience, the present author has divided these pyroxenites mineralogically into the following three groups:

1. Pyroxenites with phlogopite;
2. Feldspathic pyroxenites;
3. Werneritic pyroxenites.

The pyroxenes are from the diopside-hedenbergite series. Pyroxenes of groups 1 and 3 are nonpleochroic, while those of group 2 are the pleochroic varieties. Phlogopites are pleochroic from yellowish to greenish or reddish brown in color, with shining splendent lustre. Plagioclase feldspars (An_{52-62}) are greyish white in color, turbid and have a vitreous lustre. Wernerites are whitish grey, granular and appear to show a more or less greasy lustre. They exhibit a transition from plagioclase feldspars, evidenced by the presence of pseudomorphous twin-lamellaes.

Diverse ideas concerning the origin of these rocks have been discussed in previous regional studies (LACROIX, 1941; BESAIRIE, 1948, 1956; DE LA ROCHE, 1956, 1958; NOIZET, 1959 etc.). In general, most workers have agreed that these rocks are of metamorphic origin.

EXPERIMENTAL RESULTS

Mineral Separations

Pyroxene fractions of 99.5% purity were separated by a number of methods. The major part of pyroxene separation was performed with FORRER's Paramagnetic Separator called "Eléctrona". In cases where a completely pure separate was not obtained, "L'électro-à-pointes" (a point magnetic source) was used for final purification. In cases where even this method did not yield 99.5% pure material, heavy liquids were used for the final separations.

The samples, after crushing in an iron mortar, were screened and the 100 to 150 mesh portion was taken for separation. The fines were suspended in water and decanted. In one sample (no. 11), limonite stains were removed by boiling in dilute HCl for ten minutes. Magnetite, ilmenite, spinel and iron fillings from the iron mortar, were removed with a strong bar magnet prior to introducing the samples into the "Electrona".

At every stage of the purification process, the materials were checked or examined under a stereoscopic microscope.

Chemical Composition

The chemical analysis of the pyroxenes were carried out with an A. R. L. "Optical Emission Quantometer". The samples were crushed to 200 mesh size. Then 300 mg. of this powdered sample were mixed with 600 mg. of lithium carbonate and 3000 mg. of boric acid. The material was mixed thoroughly and fused in a platinum crucible until it became glass. This glass was ground to 200 mesh size in a mechanical ball crusher. Then 600 mg. of this powdered glass was mixed with 200 mg. of nickel oxide (internal standard) and 1200 mg. of graphite. After thorough mixing, small tablets were prepared from this material, using an A.R.L. briquetting press.

Before analyzing these samples in the quantometer, synthetic standards were prepared by mixing pure chemicals in approximately the same amounts expected in the natural samples of pyroxenes. Tablets of these standards were prepared, analyzed in the quantometer and readings were recorded. Using these readings, working curves were drawn. Tablets of the pyroxene samples were then analyzed in the quantometer, readings recorded, and the percentages of various oxides were determined from the working curves.

The conditions of the quantometer used for the analysis were as follows:

Source	A.R.L. High Precision Source (4700)
Capacity	30 F
Inductance	360 H
Resistance	45 ohms
Voltage.	950 v
Frequency.	50 cps
Time of Excitation . .	21-22 seconds.

Table 1 contains the chemical analysis of the pyroxenes. Table 2

contains the average values and analytical dispersion for sample 29 which

has been analyzed 16 times. From this, the analytical dispersion can be

judged for the other analyses. Fig. 1 gives the variations of CaO, MgO,

and Fe_2O_3 in pyroxenes.

The Ca:Mg:Fe ratios are plotted on three-point diagrams on the three-

points figure of Poldervaart and Hess (1951) which they used for the nomen-

clature of the pyroxenes. All points fall on the diopside-hedenbergite

series as shown in Fig. 2.

Fig. 3 gives the three-point diagram Al-Fe-Mg. The diagram illustrates

that, in pyroxenes from the feldspathic pyroxenites, the Fe/Al ratio is

greater than 1; and in the other pyroxenes, this ratio is less than 1. A

distinct straight line can be drawn joining the vertex of Mg and Al_{50}

in order to distinguish the pyroxenes of the feldspathic pyroxenites from

the other pyroxenes. Only pyroxene (no. 9) other than the feldspathic type

seemed to be exceptional. This pyroxene contained minute inclusions of

ilmenite and magnetite causing the Fe_2O_3 value to be greatly increased.

Optical Properties

Optical properties of the pyroxenes were systematically determined.

Results are graphically presented in Fig. 4 and tabulated in Table 3.

The refractive indices, the birefringence, the extinction angles and

the optic axial angles are plotted against the per cent Fe atoms in the

total Ca, Mg and Fe and the curves showing the variations of the optical

constants are drawn.

Observations on the measurement of specific optical properties of

these pyroxenes are summarized below.

Table I

Chemical Analysis of Pyroxenes (Major Elements)[‡]

	1	2	3	4	5	6	7	8	9
SiO_2	44.30	44.00	42.30	42.60	41.10	42.30	41.60	44.20	44.20
Al_2O_3	10.10	7.40	8.85	8.20	11.10	7.70	11.35	7.00	2.40
Fe_2O_3	5.15	5.00	7.50	7.10	5.00	11.80	6.10	3.30	21.10
CaO	25.20	25.10	23.90	24.60	25.00	24.41	24.73	24.70	20.10
MgO	14.80	15.40	15.50	14.40	14.35	12.00	14.00	17.20	8.40
MnO	0.04	0.33	0.10	00.09	0.10	0.40	0.05	0.14	1.70
TiO_2	0.42	0.43	0.38	0.36	0.67	0.24	0.58	0.30	0.06
Na_2O	0.61	0.61	0.35	0.27	0.56	0.60	0.66	0.45	0.60
Total	100.62	98.27	98.88	97.62	97.88	99.45	99.07	97.29	98.56

All of the analyses were done in quadruplicate and the average is given.

[*]: These samples were analyzed 16 times and the average is given.
n: Signifies that the element could not be analyzed.
‡: For locations see Majmundar (1961).

Table 1

Chemical Analysis of Pyroxenes (Major Elements) (Cont.)

	10	11	12	13	14	15*	16	17	18	19
SiO_2	41.50	45.35	43.20	41.10	42.00	43.52	44.40	n	46.10	45.90
Al_2O_3	8.85	2.60	2.95	4.80	5.65	7.44	5.55	7.45	2.60	4.95
Fe_2O_3	15.60	16.40	17.80	24.00	19.30	12.97	13.00	26.00	16.80	7.00
CaO	23.50	24.95	25.20	22.85	23.90	24.51	25.35	23.60	25.10	24.55
MgO	9.00	8.45	8.60	3.90	6.60	9.51	9.50	3.60	8.50	13.20
MnO	0.26	0.52	0.32	1.50	0.62	0.31	0.14	0.40	0.14	0.09
TiO_2	0.18	0.25	0.35	0.40	0.42	0.33	0.40	0.58	0.14	0.57
Na_2O	0.64	0.39	0.36	0.65	0.60	0.44	0.58	0.68	0.61	0.46
Total	99.53	98.91	98.78	99.20	99.09	99.03	99.07	-	99.99	96.63

Table 1

Chemical Analysis of Pyroxenes (Major Elements) (Cont.)

	20	21	22	23	24	25	26	27	28	29 [*]
SiO_2	44.10	43.30	43.10	41.28	47.65	41.25	44.00	n	44.50	42.30
Al_2O_3	1.60	7.10	9.30	10.15	5.90	10.10	6.75	3.00	9.20	9.88
Fe_2O_3	22.60	12.80	5.10	5.60	3.00	5.60	7.15	4.30	5.00	9.00
CaO	24.30	24.30	24.73	24.40	25.60	24.40	25.70	24.20	23.40	24.20
MgO	6.00	9.50	13.10	16.85	15.90	17.00	13.10	14.40	13.20	10.53
MnO	0.30	0.12	0.08	0.06	0.02	0.10	0.09	0.06	0.32	0.43
TiO_2	0.18	0.76	0.65	0.74	0.60	0.73	0.59	0.11	0.33	1.62
Na_2O	0.82	0.52	0.77	0.86	0.54	0.85	0.57	0.38	0.62	0.53
Total	99.90	98.40	96.83	99.94	99.21	100.03	97.95	–	96.57	98.49

Table II

Average Values and Analytical Dispersion (Major Elements)[*]

	No. of Analyses	Arithmetical Average	Coefficient of[‡] Standard Deviation	Coefficient of Relative Deviation
SiO_2	16	47.27	0.5	1.06%
Al_2O_3	16	9.84	0.8	8.13
Fe_2O_3	16	9.04	1.0	11.06
CaO	16	24.43	1.5	6.14
MgO	16	10.51	0.028	2.66
MnO	16	0.44	0.01	2.22
TiO_2	16	1.78	0.13	7.30
Na_2O	16	0.51	0.03	5.88

[*] : For sample no. 29

[‡] :
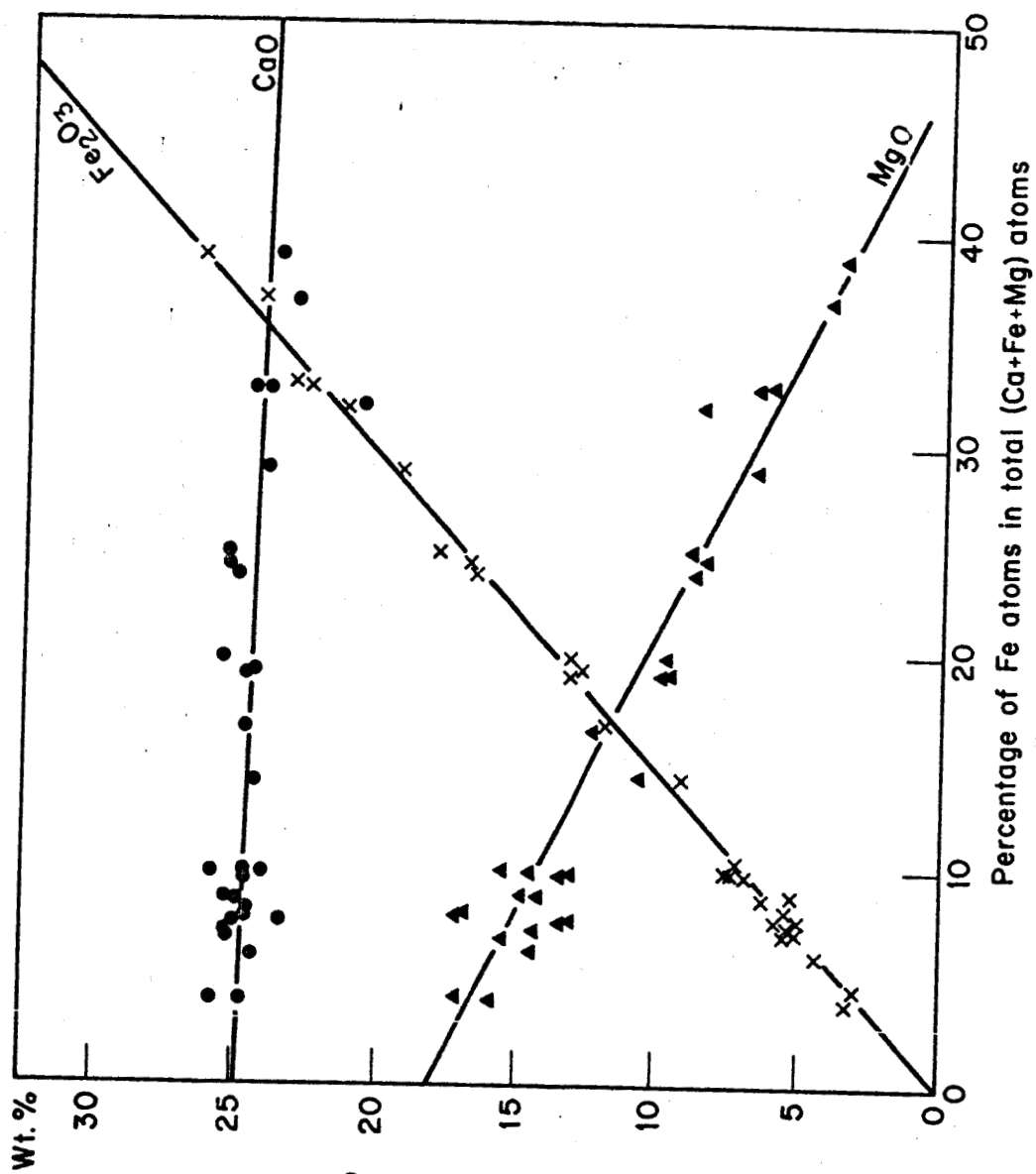$$\sigma = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n-1}}$$

Figure 1 – VARIATIONS OF CaO, MgO, AND Fe_2O_3
IN PYROXENES

Figure 2 – NOMENCLATURE OF PYROXENES (molecular per cent)
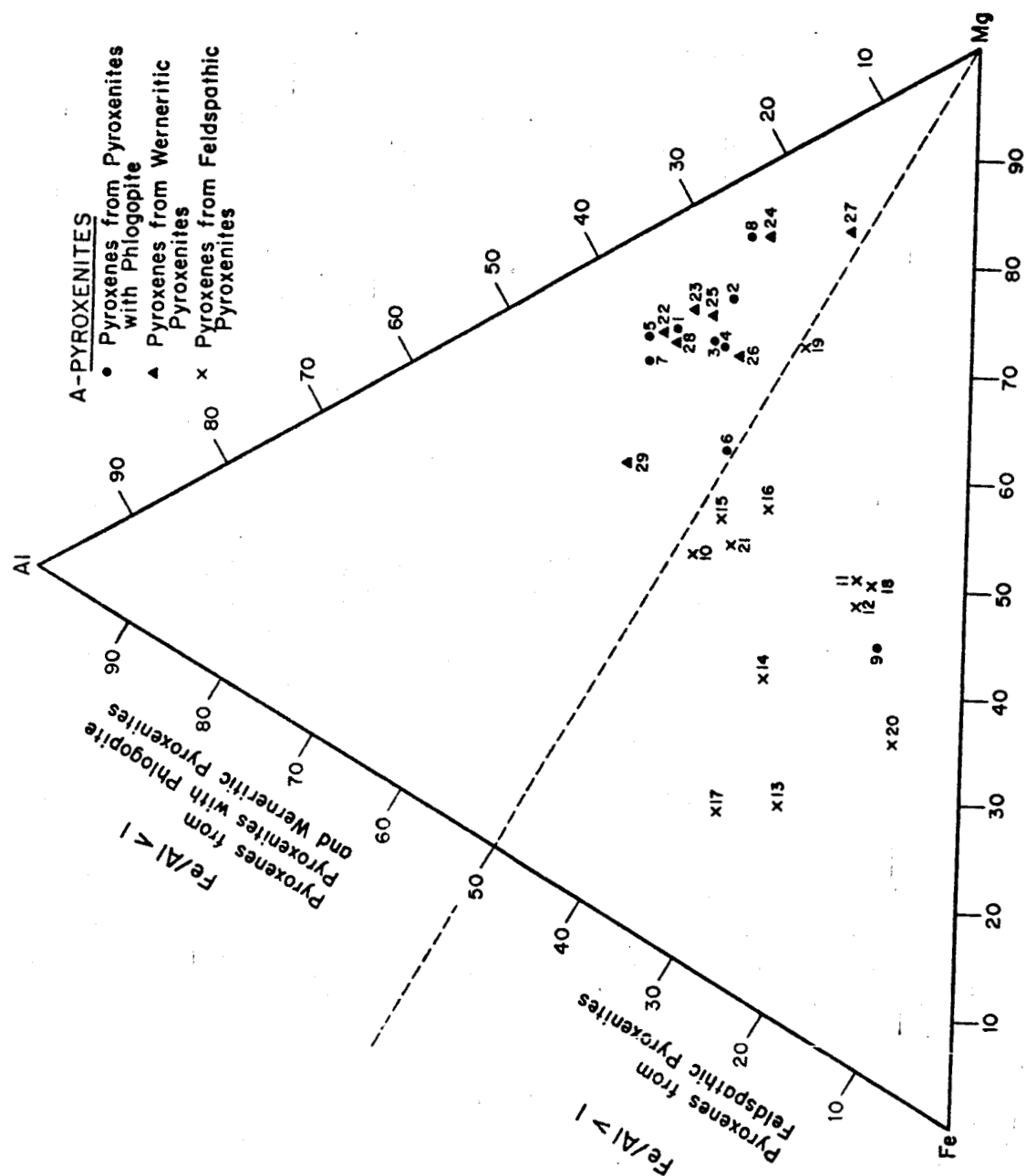AFTER POLDERVAART & HESS (1951)

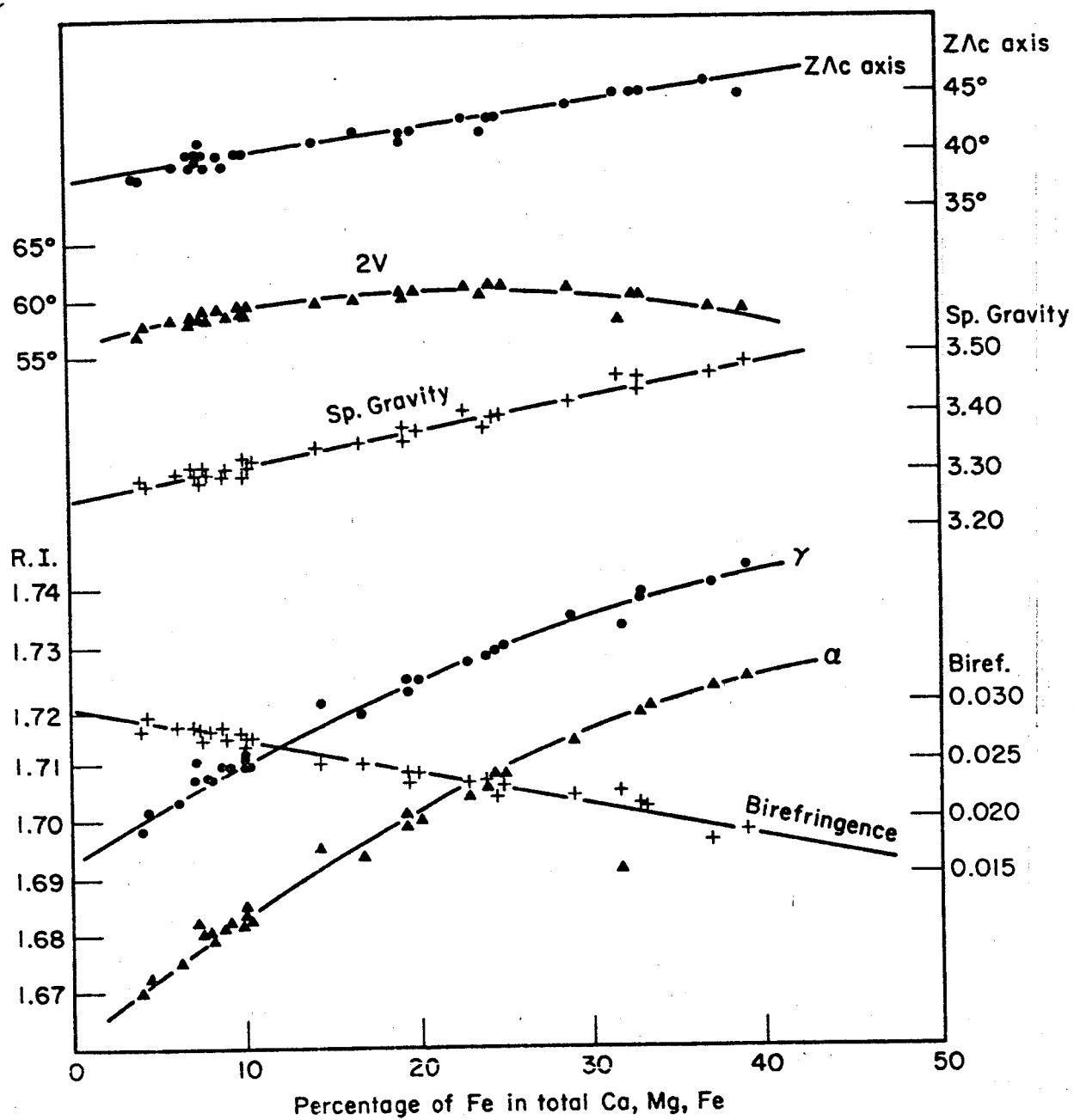Figure 3 – GEOCHEMISTRY OF PYROXENES AND MINERAL ASSOCIATIONS
(Al, Fe, Mg diagramme)

Figure 4 – RELATION OF PHYSICAL AND OPTICAL PROPERTIES AND CHEMICAL COMPOSITION IN CLINOPYROXENES

Table III

The Physical and Optical Properties of Pyroxenes

Sample No.	Sp. gravity	α	γ	Biref.	ZΛc axis	2V	Pleochroism
1	3.312	1.682	1.709	0.027	39°	58.5°(+)	Nonpleochroic
2	3.311	1.678	1.706	0.028	40°	58° (+)	Nonpleochroic
3	3.301	1.682	1.709	0.027	40°	59° (+)	Nonpleochroic
4	3.300	1.682	1.709	0.027	40°	59° (+)	Nonpleochroic
5	3.300	1.682	1.710	0.028	39°	58.5°(+)	Nonpleochroic
6	3.390	1.693	1.718	0.025	42°	60° (+)	Pleochroic (weakly)
7	3.300	1.681	1.709	0.028	40°	59° (+)	Nonpleochroic
8	3.285	1.672	1.701	0.029	38°	57.5°(+)	Nonpleochroic
9	3.462	1.690	1.712	0.022	45°	59° (+)	Pleochroic (strongly)
10	3.600	1.700	1.729	0.029	43°	61° (+)	Pleochroic
11	3.380	1.705	1.728	0.023	42°	60.5° (+)	Pleochroic
12	3.400	1.707	1.730	0.023	43°	61° (+)	Pleochroic
13	3.472	1.722	1.740	0.018	46°	59° (+)	Pleochroic
14	3.420	1.713	1.735	0.022	44°	61° (+)	Pleochroic
15	3.382	1.700	1.724	0.024	42°	60° (+)	Pleochroic
16	3.309	1.700	1.724	0.024	42°	60.5°(+)	Pleochroic
17	3.489	1.724	1.743	0.019	45°	59° (+)	Pleochroic (strongly)
18	3.398	1.707	1.729	0.022	43°	61° (+)	Pleochroic
19	3.320	1.683	1.710	0.027	40°	59° (+)	Nonpleochroic
20	3.445	1.718	1.739	0.021	45°	60° (+)	Pleochroic
21	3.391	1.699	1.722	0.023	41°	60° (+)	Pleochroic
22	3.295	1.680	1.707	0.027	40°	58.5° (+)	Nonpleochroic
23	3.300	1.680	1.708	0.028	40°	58.5°(+)	Nonpleochroic
24	3.290	1.670	1.698	0.028	38°	57° (+)	Nonpleochroic
25	3.300	1.679	1.707	0.028	39°	58.5°(+)	Nonpleochroic
26	3.310	1.684	1.711	0.027	40°	59.5°(+)	Nonpleochroic
27	3.300	1.675	1.703	0.028	39°	58° (+)	Nonpleochroic
28	3.312	1.680	1.707	0.027	41°	58.5°(+)	Nonpleochroic
29	3.345	1.695	1.720	0.025	41°	59.5°(+)	Nonpleochroic

Sample Nos 1-9 - Pyroxenites with phlogopite
10-21 - Feldspathic Pyroxenites
22-29 - Werneritic pyroxenites

Indices of Refraction

The ranges of the indices of refraction of the pyroxenes were determined by the 'Immersion Media' method. Ordinary immersion methods were used with a set of organic liquids. After a liquid or a mixture of liquids matched the index of refraction of the pyroxene, its index of refraction was determined with a Jelley's Micro-Refractometer. The value, α, varies from 1.670 to 1.724 and γ varies from 1.690 to 1.743. The normal accuracy for index determinations is estimated to be $\pm.0005$ except for material of variable composition. It is $\pm.001$ for such material.

Birefringence

An estimate of the birefringence was made using Michel Levy's principle, i.e. by determining the greatest and the least indices of refraction. The birefringence was found to vary from 0.013 to 0.029.

Extinction Angles

The extinction angles of the common clinopyroxenes vary between 38° and 46°. Methods described by TURNER (1942) and KLEEMAN (1952) were used in determining the extinction angles. A curve was obtained by plotting the results against the percentage of Fe atoms in the total Ca, Mg, Fe. Where the percentage of Fe atoms in the total Ca, Mg, Fe is zero, the extinction angle is 37.5°: and at the other end of the curve where the percentage of Fe atoms in the total Ca, Mg, Fe is 50, the extinction angle is as much as 46°.

Optic Axial Angles

All measurements of optic axial angles were made on the "Universal Stage" by direct rotation from one optic axis to the other. This method, according to HESS (1949), is more accurate than measurements of optic axial

angles by rotation from one optic axis to a bisectrix. He asserts that orientation of a grain on the "Universal Stage" to bring X, Y, Z to the vertical position cannot ordinarily be done with the accuracy usually attributed to it. In this study, the optic axial angles vary from 57° to 61° with a positive sign. These values lie on a smooth curve which has a maximum at 29 per cent Fe content. The normal accuracy, for both extinction angles and optic axial angles, is estimated to be $\pm 0.5^{\circ}$.

Pleochroism

The colors of the pyroxenes show a direct relationship to the Fe content. No other ions have been identified as affecting the transmitted color of pyroxenes, either by themselves or in conjunction with the above.

Specific Gravity

The density measurements were made by means of a pycnometer. Nearly 5 gms of the pyroxene grains, 25 ml. pycnometer bottle and distilled water were used. A curve was drawn by plotting these readings against the percentage of Fe atoms in the total Ca, Mg, Fe (Fig. 3). Results indicate that samples having a darker color and higher Fe content have higher densities. The accuracy is thought to be better than ± 0.01. All the observations were made at room temperature and are uncorrected for atmospheric pressure.

DISCUSSION

The most remarkable single characteristic of these pyroxenes is the high content of Al_2O_3 which distinguishes them from the common pyroxenes of the diopside-hedenbergite series. Common pyroxenes contain less than 3.00% Al_2O_3, but those analyzed by the author frequently contain 7.00 to 10.00% Al_2O_3. This peculiarity of the "diopsides" of S. E. Madagascar was first pointed out by LACROIX (1941), who found them to be rich in Al_2O_3

but poor in iron. He called them "Leucoaugites." Similarly, this study reveals that these pyroxenes form an isomorphous series containing a relatively high amount of Al_2O_3. Because of this, they cannot be classed in the diopside-hedenbergite series. Therefore the name "Diopsides Alumineux" (Aluminous Diopside) was given to them.

The presence of Al_2O_3 in these pyroxenes is very interesting, as it does not seem to be replaced or substituted for any of the usual elements, i.e. Ca, Mg, or Fe. In all samples analyzed, the number of Ca atoms has been found to be equal to the sum of the Fe and Mg atoms, a characteristic of the pyroxene diopside. In addition, the weight percentages of CaO, 24-26%, fall in the exact range of those found in true diopside having the formula Ca (Mg,Fe) Si_2O_6. On the contrary, however, the SiO_2 content, which would be between 49 and 55% by weight in true diopside, is comparatively low in the samples analyzed, being between 40 and 47%. So, it appears that aluminum seems to have substituted for silicon and its presence is a characteristic of these pyroxenes.

This study also reveals that color varies considerably with the proportions of major constituents. In pyroxenes having increasing amounts of iron and aluminum, the color changes from pale green to dark green or black. They show an increasing iron content, from 3.00-26.00%, with deepening of color. A reasonable assumption is that iron is the major color-control element in these minerals.

Also shown in this study is that, like iron, manganese also plays an important role as a color-control element. The darker colored pyroxenes (i.e. the most rich in iron content), also contain the higher manganese content. Likewise, there is a regular diminuation of manganese content as we progress toward the lighter colored members.

KUNO (1954) showed that the intensity of pleochroism in pyroxenes had a direct relation to the Ti content but no relation to the Fe^2 or Mn content. He further added that the strongest pleochroism is seen in the specimen having the highest Ti content, colorless pyroxenes having no Ti content. HESS (1949) also reported that the pleochroism of the clinopyroxenes is directly related to Ti and Fe^3 content. In the present study, the reverse case is noticed. There seems to be direct relationship between iron content and pleochroism. The sample showing the strongest pleochroism (sample 17) has the highest Fe content, the Ti content being very low. The pleochroism next in intensity is seen in sample 9, which has 21.10% Fe_2O_3 and the lowest content of TiO_2 (0.06%). Thus, the nonpleochroic pyroxenes have a higher Ti content and lower Fe content (samples 1, 5, 8, 26, etc.).

The indices of refraction of these pyroxenes show a similar relationship with Fe. Samples 9, 12, 13, 14, 16, 17, 20, etc., which have higher Fe contents, show higher indices of refraction. Conversely, samples having a lower Fe content had lower indices of refraction.

Similar relationships are also noticed in the densities of these pyroxenes. The pyroxenes having the higher Fe content, also have the higher densities. For example, the sample having the least Fe content has a 3.25 density and the sample having the highest Fe content has a density near 3.55.

- 19 -

Acknowledgments

The author wishes to express his sincere thanks and gratitude to Prof. MARCEL ROUBAULT, Dean, Faculty of Science, University of Nancy, France, for his kindness in giving all the facilities in the laboratories of E.N.S.G. and C.R.P.G. The author is highly obliged to Dr. H. DE LA ROCHE, Assistant Director, Center of Researches in Petrography and Geochemistry, Nancy, for his guidance throughout this study. It was he who provided the samples used in this study. The author is also indebted to Dr. GOVINDRAJU for his assistance in analytical work on the Quantometer.

REFERENCES

BESAIRIE, H. (1930) Recherches géologiques à Madagascar. D.Sc. Thesis, School of Geology, University of Toulouse, Toulouse, France.

BESAIRIE, H. (1948) Recherches géologiques à Madagascar, 2e suite, L'Extrême sud et le sud-sud-est. Tananarive, Serv. Géol. Archives, 235.

BESAIRIE, H. (1956) Le socle cristallin de Madagascar. Comm. XXe Congr. Géol. Int. Mexico (A.S.G.A.) Doc. Serv. Géol. 126, Tananarive.

HESS, H. H. (1949) Chemical composition and optical properties of common clinopyroxenes, part 1. Amer. Miner. 34, 621-666.

KLEEMAN, A. W. (1952) The determination of the extinction angle in monoclinic pyroxenes and amphiboles. Sir Douglas Mawson Anniversary volume, University of Adelaide, 101-108.

KUNO, H. (1954) Study of orthopyroxenes from volcanic rocks. Amer. Miner. 39, 30-46.

LACROIX, A. (1922) Minéralogie de Madagascar. Tom. I, II, III, Challamel, Paris.

LACROIX, A. (1941) Les gisements de phlogopite de Madagascar et les pyroxénites qui les renferment. Annal. Géol. Serv. Min. Madagascar, Fasc. XI.

MAJMUNDAR, H. (1961) Contribution à l'étude minéralogique et géochimique des pyroxènes et des micas dans les pyroxénites à phlogopite et dans les charnockites du sud-est de Madagascar. D. Sc. Thesis, School of Geology, University of Nancy, France.

NOIZET, G. (1959) Les formations de métamorphisme d'intensité elevée de l'Androy Mandrareen. Thesis, School of Geology, University of Nancy, France.

REQUEST FOR APPROVAL FOR PUBLICATION

FROM: H. H. Majmundar   DATE: Oct. 13, 1965

TO: OFFICE OF DIRECTOR

VIA: Dr. Hess
       Dr. Pieper   X 65   38004

SUBJECT: (Talk)_____ (Speaker)_____
           (Paper) New data on the optical properties and chemical composition of the
           (Report) _____ pyroxenes of S. E. Madagascar"

1. It is requested that the subject item be approved for:

   a. ☐ Presentation to: _____
                          (NAME OF ORGANIZATION OR PROFESSIONAL MEETING)

                          _____
                          (DATE OF MEETING AND CITY AND STATE)

   b. ☒ Publication in: The American Mineralogist
                          (NAME OF JOURNAL, PROCEEDINGS, ETC.)

   c. ☐ Publication as a NASA publication

2. Subject category for Goddard Journal_____ A 8 _____ Applicable only to b. and c. above.
                                                            SEE CATEGORY LIST ON REVERSE SIDE.

3. This paper (does) (does not) contain classified material.

4. This paper has been prepared keeping specifically in mind trade secrets or suggestions of outside individuals or
concerns which have been communicated to the Center in confidence, and does not violate any such disclosures, and
has been examined to see that all participating groups have been given proper credit.

5. All costs to be charged to 641-S45-01 _____ and _____
                                (JOB ORDER)   (AGENCY-WIDE CODE DESIGNATION)

_____   _____   _____
   (AUTHOR'S SIGNATURE)   (AUTHOR'S SIGNATURE)   (AUTHOR'S SIGNATURE)

BRANCH OR OFFICE HEAD COMMENT:

                                                         SIGNATURE

DIVISION CHIEF APPROVAL:

                                                         SIGNATURE

ASSISTANT DIRECTOR COMMENT:

                                                         SIGNATURE

DIRECTOR APPROVAL:

                                                         SIGNATURE

GSFC 25-9 (1/65)   John F. Clark, Acting Director

TMX# 56901